CORROSION CONTROL OF GALVANIZED STEEL IN ACIDIC MEDIUM USING PINUS OOCARPA SEED EXTRACT AS INHIBITOR

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Abstract

The potential of the seed extract of *pinus oocarpa* as an inhibitor for the corrosion of galvanized steel was studied in 2M Hydrochloric acid at 303K and 333K by gravimetric methods. Inhibition efficiency of the seed extract of *pinus oocarpa* decreased with temperature which suggests a physisorption. Synergistic effect of potassium iodide shows an increase in inhibition efficiency and synergism parameter decreased with concentration of the seed extract. The optical microscopy of galvanized steel in the presence and absence of the inhibitor reported in this study shows that the metal surface in the presence of *pinus oocarpa* seed extract was coated and cracks observed in the absence of the seed extract were filled. This observation suggests that *pinus oocarpa* seed extract can be used as coating to prevent corrosion of galvanized steel.

*Keywords: corrosion inhibitor, optical microscopy, gravimetric methods, pinus oocarpa, synergistic effect*

Introduction

Steel of different grades are used extensively in different domestic and industrial applications. It has equally been observed that industrial acid pickling and oil – well acidizing cause rapid corrosion of steel structures (Bammou et.al, 2012; Ramesh, Rajeswari and Maruthamuthu, 2003). The industry is replete with various technological attempts at proffering solutions for preventing corrosion through material selection, novel design strategies and the deployment of diverse protective techniques. The application of inhibitors as a reliable approach of protection of metallic materials from corrosion is well documented. (Khan, Ahmad and Al-Gahtan, 2017; Mobin, Parveen, Rafiquee, 2013; Afia et.al, 2011; Finšgarand, Milošev, 2010; and Breakell et al, 2005). The use of eco – friendly and biodegradable green inhibitors obtained from cheap and readily available naturally occurring extract of plant and animal origin have generated
much interest in recent times. Extracts from several plants have been reported to inhibit the corrosion of metals in acidic media (Ngbori & Kikanme, 2020; Njoku et al., 2019; Hou, Lei, Yang and Li, 2016; Nkiko, Oguntoyinbo, Bamgbose and Bamigbade, 2014; Muthukrishnan, Jeyaprabha, Prakash, 2014; Alaneme, Olusegun, 2012; Nkiko, Bamgbose, 2011).

*Pinus oocarpa* of the family pinaceae is known as egg-cone pine and it is an evergreen tree. It has been reported as a medicinal plant (Aguilar, Camacho, Chinos, Jacquez and Lopez, 1994) and it is an important commercial plant for the production of wood for the paper industry (Drovar BS, et al., 2000). Rubio, Calderon, Flores, Castrone and Cespes (2005) found that the major constituent of *pinus oocarpa* - oleoresin contains two diterpenes effective on epimastigotes of trypanosomacruzii. Philipson and Wright (1991) have shown that terpenes extracted from the plant are active against parasitic protozoans. Mohareb, Kherallah, Badawy, Salem, and Yousef (2017); de Morais, Nascimento and Melo (2005) have isolated several phytochemicals which include diterpenes, terpenophenols, sesquiterpenes, phthalates, phytools, steroids and triterpenoids. Many of these group of compounds are rich in electrons, have pi and lone pairs of electrons as well as groups that can be protonated which are features and criteria for efficient inhibition of corrosion of metals (Marzorati, Verotta and Trasatti, 2018; Friori-Bimbi, Alvarez, Vaca and Gervasi, 2015).

The present study investigated the inhibitive properties of the seed extract of *pinus oocarpa* on the corrosion of galvanized steel in Hydrochloric acid (HCl) using gravimetric method. The synergistic effect of potassium iodide (KI) on the inhibition efficiency of the extract was also analysed. Seed extract of *Pinus oocarpa* was chosen for this study because it is non-toxic, biodegradable, cheap and readily available in the Nigerian flora.

**Materials and methods**

Galvanized steel coupons of dimensions 4.5 cm by 3 cm were polished using various grades of emery paper. The polished coupons were washed with distilled water, degreased with absolute ethanol followed by acetone, dried and stored in air-tight desiccator to avoid moisture prior to use (Hernandez et al., 2012; Qiang et al., 2016). Seeds of *pinus oocarpa* were collected from the flora of the Olabisi Onabanjo University Mini- Campus, Ago- Iwoye, and classified at the Federal Research Institute of Nigeria (FRIN) FHI number 108780. The seeds were dried and ground to powder. Continuous solvent extraction was carried out with methanol. Excess
solvent was distilled and the extract left overnight to crystallize. Crystals obtained from the extract of the powdered seed were stored in air-tight desiccator and used without further purification. Inhibitor test solutions were prepared in incremental concentration of 1g (w/v) with appropriate quantity of 2M HCl in a total volume of 100 mL.

Previously prepared Galvanized Steel were weighed and immersed into 100 mL of different concentrations of the test solution.

The coupons were retrieved every 2 hours, washed and reweighed. The differences in the weight of coupons were taken as the weight loss evaluated in grams. Corrosion investigations were undertaken at two temperatures of 303K and 333K, and 2 M hydrochloric acid. The inhibition efficiency of *Pinus oocarpa* was calculated using the equation: \( I\% = \frac{(w_0 - w_i)w_0}{1} \times 100 \). The degree of surface coverage (\( \theta \)) was calculated from the equation: \( \theta = \frac{(w_0 - w_i)w_0}{1} \) and corrosion rate (mm/yr.) was evaluated using the formula, \( CR = \frac{87.6W}{\rho A t} \), Where \( W \) is the weight loss (g), \( \rho \) is the density of Galvanized Steel given as 7.85x 10g/cm-3, \( A \) is the cross-sectional area of the metal coupon and Galvanized steel (Cm²) and \( t \) is exposure time in hours. Synergistic effect of halide additive was studied by adding 10.0mM Potassium Iodide (KI), representing the concentration of KI at which the inhibitive properties of *Pinus oocarpa* seed extract is most enhanced.

**Results and Discussion**

**Weight loss and Inhibition of Efficiency of pinus oocarpa extract on corrosion of galvanized steel**

Weight loss of galvanized steel decreases with time and as the concentration of *Pinus oocarpa* extracts increases (Fig.1). Inhibition efficiency of *Pinus oocarpa* seed extracts decreases with time and increases with the concentration of extract (Fig 2). However, its inhibition efficiency decreased with increased temperature (Fig. 3). These observations presuppose that the inhibitor has covered a larger metal surface area as its concentration increases. The decrease in inhibitor efficiency as temperature increases depicts a physical mechanism of adsorption of inhibitor on the metal surface.
Corrosion rate increases with increase in temperature and decreases with inhibitor concentration (Fig. 4).

![Graph showing log Corrosion rate vs log Inhibitor concentration with data points for 303K and 333K temperatures.]

**Fig. 4:** Temperature dependence of corrosion rate with concentration of inhibitor

**Thermodynamic parameters of corrosion of galvanized steel in 2M HCl**

The surface coverage values of *pinus oocarpa* were best fitted to Langmuir model (Fig. 5) represented by the equation (1)

\[
\frac{c}{\theta} = \frac{1}{K_{ad}} + C 
\]  

(1)

The composition of seed extract of *pinus oocarpa* is complex thus its components may be attractive or repulsive towards the metal surface and adsorption may occur at the anodic or cathodic sites of the metal surface, thus the adsorption on the surface of galvanized steel is represented by the modified Langmuir shown as equation (2)

\[
\frac{c}{\theta} = \frac{1}{k_{ad}} + nC 
\]  

(2)

Where C is inhibitor concentration, \( \theta \) is the surface coverage area and n is a measure of the effectiveness of the inhibitor.
Fig. 5: Langmuir Adsorption Isotherm for the corrosion inhibition of galvanized steel in the presence of *pinus oocarpa*

Table 1: Thermodynamic parameters for the inhibition of galvanized steel by *pinus oocarpa*

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>$K_{ads}$ (kJ)</th>
<th>$n$</th>
<th>$\Delta G_{ads}$ (kJ)</th>
<th>$\Delta H_{ads}$ (kJ)</th>
<th>$\Delta S_{ads}$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>9.141</td>
<td>1.460</td>
<td>-15.692</td>
<td>-5.574</td>
<td>70.185</td>
</tr>
<tr>
<td>333</td>
<td>1.513</td>
<td>1.617</td>
<td>-12.266</td>
<td>-1.147</td>
<td>40.279</td>
</tr>
</tbody>
</table>

Table 1 shows the thermodynamic parameter obtained from the Langmuir adsorption. The free energy of adsorption obtained is negative, and less than – 20kJ/mol. The equilibrium constant $K_{ads}$ increases with temperature. The inhibitor effectiveness ‘$n$’ increases as the temperature increased from 303K to 333K. These observations suggest that *pinus oocarpa* is physical adsorbed by the metal. The enthalpy of adsorption $\Delta H_{ads}$ reported for this study is obtained from the van’t Hoff equation. The observed enthalpy of adsorption is negative and magnitude increases with temperature. This observation implies that inhibition efficie decreases as the temperature increases.
Fig. 6: Temperature dependence of Synergistic effect of 10mM KI on the inhibition efficiency of *Pinus oocarpa*.

**Optical Microscopy of Galvanized Steel in *Pinus oocarpa* extract**

Plates A–D are the optical micrographs obtained for this study using the Foundrax Brinell Microscope type 2BM15, Serial number 100332. Plates A and B is galvanized steel before and after immersion in a corrosive environment – 2M HCl respectively. Plate A seems to look smooth with minimum cracks which are further enlarged in Fig 7B. The crack observed in Plate B may have resulted from the combination of applied stress and the acidic solution. (Callister (Jr), 1997). Plate C is the micrograph of galvanized steel immersed in 2M HCl in the presence of the *Pinus oocarpa* seed extract and Plate D the micrograph of galvanized steel in the presence of inhibitor and 10mM KI. The cracks observed in Plate B appeared to have been filled significantly in Plate C and are even less pronounced due to the synergism between KI and inhibitor as shown in Plate D. This implies that *Pinus oocarpa* seed extract is an effective inhibitor and can be used as a surface coating for galvanized steel.

*Plate A: Optical Micrograph of galvanized steel before immersion in 2M HCl*
Plate B: Optical Micrograph of galvanized steel after immersion in 2M HCl

Plate C: Optical Micrograph of galvanized steel in 2M HCl, in the presence of inhibitor

Plate D: Optical Micrograph of galvanized steel in 2M HCl, in the presence of inhibitor and 10mM KI.

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Conclusion

Extract of *Pinus oocarpa* acts as an efficient inhibitor of galvanized steel. Inhibition efficiency of *Pinus oocarpa* seed extract increased with its concentration and decreased with immersion time of metal. However, its inhibition efficiency decreased as the temperature increased which presupposes a physical mechanism of adsorption. Inhibition efficiency of *Pinus oocarpa* seed extract is enhanced by addition of potassium iodide to the test solution. *Pinus oocarpa* seed extract reduces the intergranular stress cracks in galvanized steel used in this study.

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